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[54] **FRACTIONATED NOVOLAK RESIN AND PHOTORESIST COMPOSITION THEREFROM**

[75] Inventors: **M. Dalil Rahman**, Flemington; **Michelle Cook**, Somerville; **Ping-Hung Lu**, Bridgewater, all of N.J.

[73] Assignee: **Clariant Finance (BVI) Limited**, Virgin Islands (Br.)

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[56] **References Cited**

**U.S. PATENT DOCUMENTS**

5,736,292 4/1998 Ida et al. .... 430/191  
5,853,954 12/1998 Rahman et al. .... 430/270.1

*Primary Examiner*—Janet Baxter  
*Assistant Examiner*—Barbara Gilmore  
*Attorney, Agent, or Firm*—Andrew F. Sayko, Jr.

[57] **ABSTRACT**

The present invention provides a method for producing a film forming, fractionated novolak resin having consistent molecular weight and superior performance in photoresist composition, by isolating such a novolak resin fraction. A method is also provided for producing photoresist composition from such a fractionated novolak resin and for producing semiconductor devices using such a photoresist composition.

**29 Claims, No Drawings**

## FRACTIONATED NOVOLAK RESIN AND PHOTORESIST COMPOSITION THEREFROM

### BACKGROUND OF THE INVENTION

The present invention relates to a process for producing a fractionated film forming novolak resin having a fast dissolution rate, and fast photospeed and high lithographic performance in light-sensitive compositions, and for using such a novolak resin in light-sensitive compositions. The present invention also relates to a process for making a superior quality light-sensitive composition useful as a positive-working photoresist having a fast photospeed. Further, the present invention relates to a process for coating substrates with these light-sensitive compositions, as well as the process of coating, imaging and developing these light-sensitive compositions on such substrates.

Photoresist compositions are used in microlithography processes for making miniaturized electronic components, such as in the fabrication of computer chips and integrated circuits. Generally, in these processes, a thin coating of a film of a photoresist composition is first applied to a substrate material, such as silicon wafers used for making integrated circuits. The coated substrate is then baked to evaporate any solvent in the photoresist composition and to fix the coating onto the substrate. The baked coated surface of the substrate is next subjected to an image-wise exposure to radiation.

This radiation exposure causes a chemical transformation in the exposed areas of the coated surface. Visible light, ultraviolet (UV) light, electron beam and X-ray radiant energy are radiation types commonly used today in microlithographic processes. After this image-wise exposure, the coated substrate is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the coated surface of the substrate.

Novolak resins are frequently used a polymeric binder in liquid photoresist formulations. These resins are typically produced by conducting a condensation reaction between formaldehyde and one or more multi-substituted phenols, in the presence of an acid catalyst, such as oxalic acid, maleic acid, or maleic anhydride. In producing sophisticated semiconductor devices, it has become increasingly important to provide a film forming novolak resin of superior quality in terms of dissolution rate, photospeed in a photosensitive composition, better binding properties with a diazonaphthoquinone, and good heat resistance.

There are two types of photoresist compositions, negative-working and positive-working. When negative-working photoresist compositions are exposed image-wise to radiation, the areas of the resist composition exposed to the radiation become less soluble to a developer solution (e.g. a cross-linking reaction occurs) while the unexposed areas of the photoresist coating remain relatively soluble to such a solution. Thus, treatment of an exposed negative-working resist with a developer causes removal of the non-exposed areas of the photoresist coating and the creation of a negative image in the coating. Thereby uncovering a desired portion of the underlying substrate surface on which the photoresist composition was deposited.

On the other hand, when positive-working photoresist compositions are exposed image-wise to radiation, those areas of the photoresist composition exposed to the radiation become more soluble to the developer solution (e.g. a rearrangement reaction occurs) while those areas not exposed remain relatively insoluble to the developer solu-

tion. Thus, treatment of an exposed positive-working photoresist with the developer causes removal of the exposed areas of the coating and the creation of a positive image in the photoresist coating. Again, a desired portion of the underlying substrate surface is uncovered.

After this development operation, the now partially unprotected substrate may be treated with a substrate-etchant solution or plasma gases and the like. The etchant solution or plasma gases etch that portion of the substrate where the photoresist coating was removed during development. The areas of the substrate where the photoresist coating still remains are protected and, thus, an etched pattern is created in the substrate material which corresponds to the photomask used for the image-wise exposure of the radiation. Later, the remaining areas of the photoresist coating may be removed during a stripping operation, leaving a clean etched substrate surface. In some instances, it is desirable to heat treat the remaining photoresist layer, after the development step and before the etching step, to increase its adhesion to the underlying substrate and its resistance to etching solutions.

Positive working photoresist compositions are currently favored over negative working resists because the former generally have better resolution capabilities and pattern transfer characteristics. Photoresist resolution is defined as the smallest feature which the resist composition can transfer from the photomask to the substrate with a high degree of image edge acuity after exposure and development. In many manufacturing applications today, resist resolution on the order of less than one micron are necessary. In addition, it is almost always desirable that the developed photoresist wall profiles be near vertical relative to the substrate. Such demarcations between developed and undeveloped areas of the resist coating translate into accurate pattern transfer of the mask image onto the substrate.

### DESCRIPTION OF THE PRIOR ART

In the recent years there has been significant progress in novolak resin synthesis and fractionation. It has been reported that under vigorous synthetic conditions the structure of novolak resin changes, especially when high concentration of acid catalyst and high temperature is used, Rahman et al, "Rearrangement of Novolak Resin", presented at SPIE conference, 1994; Khadim et al "The Nature and Degree of Substitution Patterns in Novolaks by Carbon-13 NMR Spectroscopy", presented at SPIE conference, 1993. In a typical novolak reaction, a reactor is charged with phenolic compounds, an acid catalyst such as oxalic acid, maleic acid, p-toluene sulfonic acid or any mineral acid, and heated to about 95 to 100° C. Formaldehyde is slowly added and the mixture is heated at reflux for about 6 hours. At the end of the condensation period, the reactor is converted to distillation, and the temperature is raised to about 200° C. At this point vacuum is slowly drawn, the temperature is raised to about 220° C., and the pressure is reduced to below about 20 mm Hg. After the volatiles have been distilled off, the vacuum is released and the molten resin is collected and allowed to cool. During the course of the above resin synthesis sequence, samples are taken at various temperatures and inspected by GPC (Gel Permeation Chromatography). It was found that there was a decrease of the weight average molecular weight (all molecular weights are weight average unless otherwise specified) of the polymer, especially in the temperature range between about 160–190° C. ( Rahman et al, "The Effect of Lewis Bases on the Molecular Weight of Novolak Resins", presented at Ellenville Conference, 1994). The molecular weight

decrease (partial depolymerization) was not observed unless the phenolic compounds are extremely pure. If the phenolic compounds contain a trace amount of a Lewis Base, such as a nitrogen base, the molecular weight decrease during the distillation process was not observed. In U.S. Pat. No. 5,476,750, assigned to the same assignee as the subject application and incorporated herein by reference, an improved process is disclosed to control molecular weight (avoid substantial depolymerization) by adjusting the amount of Lewis Base in the phenolic compounds before or after the condensation reaction. It was disclosed that during the purification process of such phenolic compounds using an ion exchange resin, distillation, and/or a solvent extraction process, to remove metal ions, the minor amount of Lewis Base present was also removed. Due to the absence of this base, the novolak resin was partially depolymerized during the manufacturing process. The physical properties of the depolymerized resin changed due to degradation, and it was not useful for photoresist compositions. This problem can be substantially avoided by adjusting the level of Lewis Base before or after the condensation step of the novolak resin manufacturing process.

In copending U.S. patent application Ser. No. 366,634, filed on Dec. 30, 1994, (WO 96/21211 published Jul. 11, 1996) assigned to the same assignee as the subject application and incorporated herein by reference, an improved process is disclosed for isolating a novolak resin at a temperature less than about 140° C. by using subsurface forced steam distillation to avoid high temperature molecular weight breakdown of the resin. (Rahman et al, "Isolation of Novolak Resin at Low Temperature", presented at SPIE Conference, 1996.) It is known that a film forming novolak resin can be made by the condensation reaction of a mixture of phenolic monomers with an aldehyde source. Such novolak resin synthesis processes are disclosed in U.S. Pat. No. 5,346,799, incorporated herein by reference.

#### SUMMARY OF THE INVENTION

The present invention relates to a process for producing a fractionated film forming novolak resin having a fast dissolution rate, with fast photospeed and high lithographic performance in light-sensitive compositions, and for using such a novolak resin in light-sensitive compositions. The present invention also relates to a process for making a superior quality light-sensitive composition useful as a positive-working photoresist having a fast photospeed. This can be accomplished by reacting substituted phenols and formaldehyde in the presence of an acid catalyst and, after distillation, isolating the synthesized novolak resin in a photoresist solvent, such as ethyl lactate, and adding a water soluble organic polar solvent, such as acetone, dimethylformamide (DMF), dimethylsulfoxide, tetrahydrofuran (THF), ethylene glycol or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol, such as ethanol, propanol or, preferably, methanol. Water, preferably deionized (DI) water, is also added, thereby separating the solution into two solution phases (layers). The top phase is water and water-soluble organic polar solvent having low molecular weight novolak resin dissolved in it. The bottom phase is a photoresist solvent having high molecular weight novolak resin dissolved in it. The top phase is then separated from the bottom phase, such as by suction or by siphoning, thereby removing the low molecular weight novolak resin fraction. To the bottom phase are then added, preferably with stirring, additional water-soluble organic polar solvent and water, preferably DI water. The two phases are again separated in the same manner and the top phase is removed, such as by suction or by siphoning, thereby removing more low

molecular weight novolak resin. The high molecular weight novolak resin in the bottom phase is then separated, such as by distilling under vacuum to remove residual water and water-soluble organic polar solvent, and the high molecular weight novolak resin fraction is then dissolved in a photoresist solvent.

The photoresist solvent may comprise propylene glycol methyl ether acetate, 3-methoxy-3-methyl butanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, ethylene glycol monomethyl acetate, methyl ethyl ketone, 2-heptanone or a monooxymonocarboxylic acid ester, such as methyl oxyacetate, ethyl oxyacetate, butyl oxyacetate, methyl methoxyacetate, ethyl methoxyacetate, butyl methoxyacetate, methyl ethoxyacetate, ethyl ethoxyacetate, ethoxy ethyl propionate, methyl 3-oxypropionate, ethyl 3-oxypropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 2-oxypropionate, ethyl 2-oxypropionate, ethyl 2-hydroxypropionate (ethyl lactate), ethyl 3-hydroxypropionate, propyl 2-oxypropionate, methyl 2-ethoxypropionate, or propyl 2-methoxy propionate, or mixtures of one or more of these solvents.

The present invention relates to a process for fractionating a novolak resin to provide a film forming novolak resin having a high dissolution rate, and a fast photospeed and high lithographic performance in light-sensitive compositions. The invention also relates to a process for producing a photoresist composition containing such a novolak resin. The invention further relates to a process for producing semiconductor devices using such photoresists containing such a novolak resin, photoresist solvent(s), and a photosensitizer.

Film forming novolak resins may be obtained by condensing formaldehyde and one or more phenolic compounds, such as m-cresol, p-cresol, 2,4- and 2,5-dimethylphenol, 3,5-dimethylphenol, or 2,3,5-trimethylphenol, resorcinol, 2-methyl resorcinol, 5-methylresorcinol. The condensation reaction is normally carried out in the presence of an acid catalyst, such as oxalic acid, maleic acid, maleic anhydride, p-toluene sulfonic acid or sulfuric acid.

In the process of the present invention a novolak resin having a high dissolution rate, and a fast photospeed and superior lithographic performance in photoresist compositions is obtained. The present invention provides a process for producing a film forming novolak resin, which process comprises:

- a) condensing (reacting) formaldehyde or its equivalent, such as paraformaldehyde or formalin, with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin condensation product, removing unreacted substituted phenols, such as by distilling the novolak resin condensation product under atmospheric pressure and then under vacuum at high temperature;
- b) adding a photoresist solvent, then a water soluble organic polar solvent, and water, preferably DI water, to the novolak resin condensation product resulting from step a), at a ratio of photoresist solvent:water soluble organic polar solvent:water of 1-9:1-5:3-7, preferably 6-9:1-3:3-5 and thereby forming a solution of the novolak resin condensation product and separating the solution into two layers, a top layer solution and a bottom layer solution, and then removing the top layer, which comprises a solution of unreacted phenolic compounds, low molecular weight novolak resin, and useless monomer and oligomers, such as by decanting or by suction;

- c) adding a water soluble organic polar solvent and water to the bottom layer solution remaining after step b), in the ratio of water soluble organic polar solvent:water ratio of 1:10 to 10:1, preferably 2:8 to 8:2, more preferably 3:7 to 7:3, and most preferably 4:6 to 6:4, thereby separating the bottom layer solution from step b) into two layers, a top layer solution and a bottom layer solution, and then removing the top layer, such as by decanting or by suction;
- d) removing any remaining water and water soluble organic polar solvent from the bottom layer solution resulting from step c), such as by distilling the solution of novolak resin under vacuum and low temperature, adding a photoresist solvent to the novolak resin, and thereby producing a film forming, fractionated novolak resin solution.

The present invention further provides a process for producing a positive photoresist composition having superior lithographic performance. The subject process comprises:

- a) condensing (reacting) formaldehyde or its equivalent, such as paraformaldehyde or formalin, with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin condensation product, removing unreacted substituted phenols, such as by distilling the novolak resin condensation product under atmospheric pressure, and then under vacuum at high temperature;
- b) adding a photoresist solvent, then a water soluble organic polar solvent, and water, preferably DI water, to the novolak resin condensation product resulting from step a), at a ratio of photoresist solvent:water soluble organic polar solvent:water of 1-9:1-5:3-7, preferably 6-9:1-3:3-5, and thereby forming a solution of the novolak resin condensation product and separating the solution into two layers, a top layer solution and a bottom layer solution, and then removing the top layer, which comprises a solution of unreacted phenolic compounds, low molecular weight novolak resin, and useless monomer and oligomers, such as by decanting or by suction;
- c) adding a water soluble organic polar solvent and water to the bottom layer solution remaining after step b), in the ratio of water soluble organic polar solvent:water ratio of 1:10 to 10:1, preferably 2:8 to 8:2, more preferably 3:7 to 7:3, and most preferably 4:6 to 6:4, thereby separating the bottom layer solution from step b) into two layers, a top layer solution and a bottom layer solution, and then removing the top layer, such as by decanting or by suction;
- d) removing any remaining water and water soluble organic polar solvent from the bottom layer solution resulting from step c), such as by distilling the solution of novolak resin under vacuum and low temperature, adding a photoresist solvent to the novolak resin, and thereby producing a film forming, fractionated novolak resin solution;
- e) providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize a photoresist composition; 2) the film forming novolak resin solution resulting from step d); and 3) additional photoresist solvent, and thereby forming a photoresist composition.

The invention further provides a method for producing a semiconductor device by producing a photo-image on a substrate by coating a suitable substrate with a positive working photoresist composition. The subject process comprises:

- a) condensing (reacting) formaldehyde or its equivalent, such as paraformaldehyde or formalin, with one or more

- phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin condensation product, removing unreacted substituted phenols, such as by distilling the novolak resin condensation product under atmospheric pressure and then under vacuum at high temperature;
- b) adding a photoresist solvent, then a water soluble organic polar solvent, and water, preferably DI water, to the novolak resin condensation product resulting from step a), at a ratio of photoresist solvent: water soluble organic polar solvent:water of 1-9:1-5:3-7, preferably 6-9:1-3:3-5, and thereby forming a solution of the novolak resin condensation product and separating the solution into two layers, a top layer solution and a bottom layer solution, and then removing the top layer, which comprises a solution of unreacted phenolic compounds, low molecular weight novolak resin, and useless monomer and oligomers, such as by decanting or by suction;
- c) adding a water soluble organic polar solvent and water to the bottom layer solution resulting from step b), in the ratio of water soluble organic polar solvent:water ratio of 1:10 to 10:1, preferably 2:8 to 8:2, more preferably 3:7 to 7:3, and most preferably 4:6 to 6:4, thereby separating the bottom layer solution from step b) into two layers, a top layer solution and a bottom layer solution, and then removing the top layer, such as by decanting or by suction;
- d) removing any remaining water and water soluble organic polar solvent from the bottom layer resulting from step c), such as by distilling the solution of novolak resin under vacuum and low temperature, adding a high boiling solvent to the novolak resin, and thereby producing a film forming, fractionated novolak resin solution;
- e) providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize a photoresist composition; 2) the film forming, fractionated novolak resin solution resulting from step d); and 3) additional photoresist solvent, and thereby forming a photoresist composition;
- f) coating a suitable substrate with the photoresist composition resulting from step e);
- g) heat treating the coated substrate resulting from step f) until substantially all of the high boiling solvent and photoresist solvent is removed; image-wise exposing the photosensitive composition and removing the image-wise exposed areas of such composition with a suitable developer, such as an aqueous alkaline developer. Optionally one may also perform a baking of the substrate either immediately before or after the removing step.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Novolak resins have been commonly used in the art of photoresist manufacture as exemplified by "Chemistry and Application of Phenolic Resins", Knop A. And Scheib, W.; Springer Verlag, New York, 1979 in Chapter 4. Similarly, o-quinone diazides are well known to the skilled artisan as demonstrated by "Light Sensitive Systems", Kosar, J.; John Wiley & Sons, New York, 1965 Chapter 7.4. However, the instant invention has found that the use of particular resins isolated without high temperature distillation, as opposed to those taught in the prior art, produces a photoresist having a superior resolution and depth of focus.

Optional ingredients for the photoresist compositions of the present invention include colorants, dyes, anti-striation agents, leveling agents, plasticizers, adhesion promoters, speed enhancers, solvents and such surfactants as non-ionic

surfactants, which may be added to the solution of novolak resin, sensitizer and solvent before the photoresist composition is coated onto a substrate. Examples of dye additives that may be used together with the photoresist compositions of the present invention include Methyl Violet 2B (C.I. No. 42535), Crystal Violet (C.I. 42555), Malachite Green (C.I. No. 42000), Victoria Blue B (C.I. No. 44045) and Neutral Red (C.I. No. 50040) at one to ten percent weight levels, based on the combined weight of novolak and sensitizer. The dye additives help provide increased resolution by inhibiting back scattering of light off the substrate.

Anti-striation agents may be used at up to about a five percent weight level, based on the combined weight of novolak and sensitizer. Plasticizers which may be used include, for example, phosphoric acid tri-(beta-chloroethyl)-ester; stearic acid; dicamphor; polypropylene; acetal resins; phenoxy resins; and alkyl resins, at about one to ten percent weight levels, based on the combined weight of novolak and sensitizer. The plasticizer additives improve the coating properties of the material and enable the application of a film that is smooth and of uniform thickness to the substrate.

Adhesion promoters which may be used include, for example, beta-(3,4-epoxy-cyclohexyl)-ethyltrimethoxysilane; p-methyl-disilane-methyl methacrylate; vinyl trichlorosilane; and gamma-amino-propyl triethoxysilane, up to about a 4 percent weight level, based on the combined weight of novolak and sensitizer. Development speed enhancers that may be used include, for example, picric acid, nicotinic acid or nitrocinnamic acid up to about a 20 percent weight level, based on the combined weight of novolak and sensitizer. These enhancers tend to increase the solubility of the photoresist coating in both the exposed and unexposed areas, and thus they are used in applications when speed of development is the overriding consideration even though some degree of contrast may be sacrificed; i.e., while the exposed areas of the photoresist coating will be dissolved more quickly by the developer, the speed enhances will also cause a larger loss of photoresist coating from the unexposed areas.

The photoresist solvent(s) may be present in the overall photoresist composition in an amount of up to 95% by weight of the solids in the composition. Solvents, of course are substantially removed after coating of the photoresist solution on a substrate and subsequent drying. Non-ionic surfactants that may be used include, for example, nonylphenoxy poly(ethyleneoxy) ethanol; octylphenoxy ethanol at up to about 10% weight levels, based on the combined weight of novolak and sensitizer.

The prepared photoresist solution, can be applied to a substrate by any conventional method used in the photoresist art, including dipping, spraying, whirling and spin coating. When spin coating, for example, the resist solution can be adjusted with respect to the percentage of solids content, in order to provide coating of the desired thickness, given the type of spinning equipment utilized and the amount of time allowed for the spinning process. Suitable substrates include silicon, aluminum, polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds.

The photoresist coatings produced by the described procedure are particularly suitable for application to thermally grown silicon/silicon dioxide-coated wafers, such as are utilized in the production of microprocessors and other miniaturized integrated circuit components. An aluminum/aluminum oxide wafer can also be used. The substrate may

also comprise various polymeric resins, especially transparent polymers such as polyesters. The substrate may have an adhesion promoted layer of a suitable composition, such as one containing hexa-alkyl disilazane, preferably hexamethyl disilazane (HMDS).

The photoresist composition solution is then coated onto the substrate, and the substrate is treated at a temperature from about 70° C. to about 110° C. for from about 30 seconds to about 180 seconds on a hot plate or for from about 15 to about 90 minutes in a convection oven. This temperature treatment is selected in order to reduce the concentration of residual solvents in the photoresist, while not causing substantial thermal degradation of the photosensitizer. In general, one desires to minimize the concentration of solvents and this first temperature treatment is conducted until substantially all of the solvents have evaporated and a thin coating of photoresist composition, on the order of one micron in thickness, remains on the substrate. In a preferred embodiment the temperature is from about 85° C. to about 95° C. The treatment is conducted until the rate of change of solvent removal becomes relatively insignificant. The temperature and time selection depends on the photoresist properties desired by the user, as well as the equipment used and commercially desired coating times. The coated substrate can then be exposed to actinic radiation, e.g., ultraviolet radiation, at a wavelength of from about 300 nm (nanometers) to about 450 nm, x-ray, electron beam, ion beam or laser radiation, in any desired pattern, produced by use of suitable masks, negatives, stencils, templates, etc.

The photoresist is then optionally subjected to a post exposure second baking or heat treatment, either before or after development. The heating temperatures may range from about 90° C. to about 120° C., more preferably from about 100° C. to about 110° C. The heating may be conducted for from about 30 seconds to about 2 minutes, more preferably from about 60 seconds to about 90 seconds on a hot plate or about 30 to about 45 minutes in an oven.

The exposed photoresist-coated substrates are developed to remove the image-wise exposed areas by immersion in an alkaline developing solution or developed by a spray development process. The solution is preferably agitated, for example, by nitrogen burst agitation. The substrates are allowed to remain in the developer until all, or substantially all, of the photoresist coating has dissolved from the exposed areas. Developers may include aqueous solutions of ammonium or alkali metal hydroxides. One preferred hydroxide is tetramethyl ammonium hydroxide. After removal of the coated wafers from the developing solution, one may conduct an optional post-development heat treatment or bake to increase the coating's adhesion and chemical resistance to etching solutions and other substances. The post-development heat treatment can comprise the oven baking of the coating and substrate below the coating's softening point. In industrial applications, particularly in the manufacture of microcircuitry units on silicon/silicon dioxide-type substrates, the developed substrates may be treated with a buffered, hydrofluoric acid base etching solution. The photoresist compositions of the present invention are resistant to acid-base etching solutions and provide effective protection for the unexposed photoresist-coating areas of the substrate.

The following specific examples will provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as

providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

#### EXAMPLE 1

300 grams of phenolic compounds consisting of a cresol (phenolic compound) ratio of 5/4/2/0.25 using 127.06 grams of m-cresol, 101.64 grams of p-cresol, 64.00 grams of 2,3,5-trimethyl phenol, 7.29 grams of 2-methyl resorcinol, and 58.9 grams of paraformaldehyde (molar ratio of phenols/paraformaldehyde 1/0.70) were transferred to a four necked flask equipped with a condenser, a thermometer, and a dropping funnel. 0.9 grams of oxalic acid were added and the flask was heated to 95° C. There was an exotherm, which raised the temperature to 110° C., and 20 grams of room temperature DI water were added to combat the exotherm. The reaction ran at condensation for 3 hours. The reaction mixture was then distilled, initially under atmospheric pressure at 175° C., then vacuum was applied and the reaction was distilled for 5 minutes at 200° C. and 25 mm Hg. After vacuum distillation, at ~180° C., 658 grams of ethyl lactate were added to make approximately a 30% solids solution. After the resin was cooled to room temperature a sample was taken for GPC MW<sub>w</sub> measurement. 235 grams of acetone were then added to make a 24% solids solution. 42.9% (w/w) water (504 g) was then added to the 24% resin solution and 2 layers were formed, a top layer and a bottom layer. The top layer was siphoned off. Samples of both the siphoned top layer and the remaining bottom layer were given for GPC MW<sub>w</sub> measurement. ½ the original amount of acetone (117.5 g) was added to the resin/ethyl lactate and stirred. Then ½ the starting amount of water (252 g) was added to form 2 layers. The top layer was siphoned off, a sample taken for GPC-MW, and the bottom layer was distilled to achieve ~30% solids. All GPC MW<sub>w</sub> data are compiled in Table 1 below.

TABLE 1

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	3706	4.50
1st siphon layer (top)	2071	6.18
1st fractionation (resin/bottom layer)	4400	3.96
2nd siphon layer (top)	1416	11.27
fine tuned fraction	4557	3.79

Polydispersity = MW<sub>w</sub>/MW<sub>N</sub>

#### EXAMPLE 2

A 50 gram photoresist test sample was prepared according to the following formulation:

NK-280 (a proprietary 2,1,5-diazonaphthoquinone sulfonyl chloride based sensitizer from Nippon Zeon Co)	2.02 gm
NK-240 (a proprietary 2,1,4-diazonaphthoquinone sulfonyl chloride based sensitizer from Nippon Zeon Co.)	0.84 gm
Novolak Resin fraction from example #1	6.80 gm
Bl26X-SA (a proprietary speed enhancer from Nippon Zeon Co.)	1.203 gm
KP-341, a striation free surfactant from Shinetsue Chem. Co. (2% in Ethyl Lactate)	0.004 gm
Ethyl Lactate	33.147 gm
n-Butyl Acetate	5.849 gm

The photoresist resist sample was coated on an hexamethyldisilazane (HMDS) primed silicon wafer to 1.083 μm

film thickness, and a soft bake at 90° C. for 60 seconds on an SVG® 8100 I-line hot plate was used. The exposure matrix was printed on the coated wafers using a 0.54 NA NIKON® i-line stepper and a NIKON® resolution reticle.

5 The exposed wafers were PEB (post exposure baked) at 110° C. for 70 seconds on an in line hot plate. The wafers were then developed using AZ® 300 MIF TMAH (tetramethyl ammonium hydroxide—2.38%) developer. The developed wafers were examined using a HITACHI® S-400 SEM (scanning electron microscope). A nominal dose (Dose to Print, "DTP") in millijoules (mj) was measured at the best focus, the dose required to precisely replicate a given feature. Resolution and depth of focus (DOF) in micrometers (microns, μm) were measured and are shown in Table 10.

#### EXAMPLE 3

The condensation reaction in example 1 was repeated using 500 grams of phenolic compounds in the ratio of 5/4/1/1 with 219.15 grams of meta cresol, 175.32 grams of para cresol, 55.19 grams of 2,3,5-trimethylphenol, 50.32 grams of 2-methylresorcinol, 96.56 grams paraformaldehyde(cresol/aldehyde 1/0.685), and 1.5 grams of oxalic acid as the catalyst. After condensation and distillation, at ~180° C., 1096 grams of ethyl lactate were added to provide a 30% solids solution, and a sample was taken for GPC-MW<sub>w</sub>. 322.8 grams of acetone were then added to get a 24% solids solution. Then 860.04 grams (46.5%w/w) DI water were added to provide the 2 separate top and bottom layers. The rest of the process again followed example 1 with an appropriate amounts of the second acetone and water additions. The GPC-MW<sub>w</sub> data is shown in Table 3 below:

TABLE 2

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	4362	2.46
1st siphon layer (top)	2527	1.81
1st fractionation (resin/bottom layer)	6014	2.64
resin isolated from 2nd siphon layer	3927	2.40
after distillation (top)		
fine tuned fraction	5621	2.54

#### EXAMPLE 4

A 150 gram photoresist test sample was prepared according to the following formulation:

NK-280 (a proprietary 2,1,5-diazonaphthoquinone sulfonyl chloride based sensitizer from Nippon Zeon Co)	26.07 gm
NK-240 (a proprietary 2,1,4-diazonaphthoquinone sulfonyl chloride based sensitizer from Nippon Zeon Co.)	2.51 gm
Novolak Resin fraction from example #3	20.313 gm
Pyrogallol from Aldrich Co.	0.49 gm
Bl26X-SA (a proprietary speed enhancer from Nippon Zeon Co.)	3.61 gm
KP-341, a striation free surfactant from Shinetsue Chem. Co. (2% in Ethyl Lactate)	0.012 gm
Ethyl Lactate	99.44 gm
n-Butyl Acetate	17.55 gm

The photoresist resist sample was coated on an HMDS primed silicon wafer to a 1.083 μm film thickness, and a soft bake at 90° C. for 60 seconds on an SVG® 8100 I-line hot plate was used. The exposure matrix was printed on the coated wafers using a 0.54 NA NIKON® i-line stepper and

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a NIKON® resolution reticle. The exposed wafers were post exposure baked at 110° C. for 70 seconds on an in line hot plate. The wafers were then developed using AZ® 300 MIF TMAH (2.38%) developer. The developed wafers were examined using a HITACHI® S-400 SEM. A nominal dose (DTP) was measured at the best focus, the dose required to precisely replicate a given feature. Resolution and depth of focus (DOF) were measured and were shown in Table 10.

## EXAMPLE 5

The condensation reaction in example 1 was repeated using 150 grams of cresols in the ratio of 5/4/2/0.25 with 63.5 grams of meta cresol, 50.8 grams of para cresol, 32 grams of 2,3,5-trimethylphenol, 3.65 grams of 2-methylresorcinol, 29.5 grams paraformaldehyde(cresol/aldehyde 1/0.7), and 0.15 grams of oxalic acid catalyst. After condensation and distillation, at ~180° C. 330.75 grams of ethyl lactate were added to achieve a 30% solids solution, and a sample was taken for GPC-MW<sub>w</sub>. 115.5 grams of methanol were then added to get a 24% solids solution. Then 252.04 grams (42.9%w/w) DI water were added to provide the 2 separate top and bottom layers. The rest of the process again followed example 1 with appropriately different amounts of the second methanol and water additions. The GPC-MW<sub>w</sub> data is shown in Table 7 below:

TABLE 3

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	2587	4348
1st siphon layer (top)	1461	3.18
1st fractionation (resin/bottom layer)	3249	4.43
2nd siphon layer (top)	516	2.21
fine tuned fraction	3341	3.36

## EXAMPLE 6

The condensation reaction in example 5 was repeated using 300 grams of cresols in the ratio of 5/4/2/0.3 with 126.44 grams of meta cresol, 101.16 grams of para cresol, 63.69 grams of 2,3,5-trimethylphenol, 8.71 grams of 2-methylresorcinol, 57.63 grams paraformaldehyde(cresol/aldehyde 1/0.69), and 0.9 grams of oxalic acid catalyst. After condensation and distillation, at ~180° C., 658 grams of ethyl lactate were added to achieve 30% solids, and a sample was taken for GPC-MW. 205.82 grams of Methanol were then added to get a 24% solids solution. Then 449.29 grams (41% w/w) DI water were added to get the 2 layers. The rest of the process again followed example 5 with just different amounts of the second methanol and water additions. The GPC-MW data is shown in Table 5.

TABLE 4

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	3136	4.76
1st siphon layer (top)	2179	4.23
1st fractionation (resin/bottom layer)	3944	4.60
2nd siphon layer (top)	481	2.79
fine tuned fraction	3948	4.89

## EXAMPLE 7

Example 6 was repeated with a phenolic compound (m-cresol, p-cresol, 2,3,5-trimethyl phenol, and 2-methyl resorcinol) ratio of 5/4/2/0.35 and a cresol paraformalde-

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hyde ratio of 1/0.69 using the exact conditions and 40% (w/w) water was added for fractionation. GPC MW<sub>w</sub> data are shown below in Table 5.

TABLE 5

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	4197	3.86
1st siphon layer (top)	2878	3.22
1st fractionation (resin/bottom layer)	5465	3.92
2nd siphon layer (top)	689	2.66
fine tuned fraction	5517	3.41

## EXAMPLE 8

Example 7 was repeated using the same cresol and paraformaldehyde ratio. After condensation, however, a minimum amount of ethyl lactate-28 grams(10% by weight of the resin) was added. The resin cooled very quickly, and the resin solution became very thick. 868 grams of methanol were added to make a 24% solids solution. 329.1 grams of the resin solution were transferred to another flask and 28% w/w water was added to provide the 2 separate top and bottom layers. The top layer was siphoned off and a sample was taken of both the resin/bottom layer and the siphon layer (top) for GPC MW<sub>w</sub> analysis. Then ½ the estimated amount of methanol in the starting solution was added to redissolve the resin. ½ the amount of starting water was added to the resin solution to provide the 2 separate top and bottom layers. The top layer was siphoned off and a sample was taken for GPC MW<sub>w</sub>. Ethyl lactate was added to the remaining resin/bottom layer and the dissolved resin solution was distilled at 75° C. and 25 mm Hg to remove residual water and methanol, and to achieve the correct % solids. The GPC MW<sub>w</sub> data are shown below in Table 6.

TABLE 6

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	3207	3.48
1st siphon layer (top)	1415	2.30
1st fractionation (resin/bottom layer)	4456	4.23
2nd siphon layer (top)	1292	1.82
fine tuned fraction	4766	3.53

## EXAMPLE 9

The remaining resin/bottom layer from example 8 was distilled at 75° C. and 25 mm Hg to try to remove the methanol. The % solids was checked in ethyl lactate and then adjusted to 30% solid in ethyl lactate by adding additional ethyl lactate. 212 grams of methanol were added to provide a 24% solids solution. To this new resin solution 38% (w/w) water was added to provide 2 separate top and bottom layers. The top layer was siphoned off and samples were taken from both top and bottom layers for GPC MW<sub>w</sub>. ½ the original amount of methanol was added to the ethyl lactate resin/bottom layer and then ½ the original amount of water was added to provide 2 separate top and bottom layers. The top layer was siphoned off and a sample was taken for GPC MW. Ethyl lactate was added to the resin/bottom layer and the redissolved resin was distilled at 75° C. and 25 mm Hg to remove residual water, methanol, and to achieve the correct % solids. The GPC MW<sub>w</sub> data are shown below in Table 7.

TABLE 7

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	3207	3.48
1st siphon layer (top)	2940	1.95
1st fractionation (resin/bottom layer)	4749	2.41
2nd siphon layer (top)	1426	1.35
fine tuned fraction	4809	2.30

## EXAMPLE 10

Example 6 was repeated with a phenolic compound (m-cresol, p-cresol, 2,3,5-trimethyl phenol, and 2-methyl resorcinol) ratio of 5/4/2/0.3 and a cresol paraformaldehyde ratio of 1/0.685 using the exact conditions and 44% (w/w) water was added for fractionation. GPC MW<sub>w</sub> data are shown below in Table 8.

TABLE 8

Description	GPC-MW <sub>w</sub>	Polydispersity
sample after condensation	3542	3.87
1st siphon layer (top)	2121	3.22
1st fractionation (resin/bottom layer)	4430	3.90
2nd siphon layer (top)	690	2.86
fine tuned fraction	4443	3.80

## EXAMPLE 11

Example 6 was repeated with a phenolic compound (m-cresol, p-cresol, 2,3,5-trimethyl phenol, and 2-methyl resorcinol) ratio of 5/4/2/0.35 and a cresol paraformaldehyde ratio of 1/0.69 using the exact conditions and 38% (w/w) water was added for fractionation. GPC MW<sub>w</sub> data are shown below in Table 9.

TABLE 9

Description	GPC-MW <sub>w</sub>	Polydispersity
1st siphon layer (top)	2963	2.11
1st fractionation (resin/bottom layer)	4365	2.41
2nd siphon layer (top)	755	1.46
fine tuned fraction	4540	2.40

## EXAMPLES 12 to 15

Example 4 was repeated with resins from examples 8, 9, 10 and 11 to formulate photoresist compositions as example 4 to create examples 12 to 15. The photo lithographic evaluation data are shown in Table 10.

TABLE 10

Example	Resin From:	DTP mj	Resolution $\mu\text{m}$	DOF $\mu\text{m}$
2	Example 1	165	0.34	(-.8/0.4)
4	Example 3	225	0.32	(-.1/0.2)
12	Example 8	205	0.32	(-1.0/-0.25)
13	Example 9	160	0.32	(-1.0/0.25)
14	Example 10	150	0.32	(-0.8/0.2)
15	Example 11	110	0.32	(-0.8/0.2)

## COMPARATIVE EXAMPLE

300 grams of phenolic compounds consisting of a cresol ratio 5/4/2, using 130.26 grams of m-cresol, 104.9 grams of

p-cresol, 65.59 grams of 2,3,5-trimethyl phenol, and 58.64 grams of paraformaldehyde (molar ratio of phenols/paraformaldehyde 1/0.70) were transferred to a four necked flask equipped with a condenser, a thermometer, and a dropping funnel containing 100 grams of DI water. 0.9 gram of oxalic acid catalyst was added and the flask was heated to 95° C. There was an exotherm to 112° C. and ~22 grams of DI water were to combat the exotherm. The reaction ran at condensation for 3 hours. The reaction mixture was then distilled, initially under atmospheric pressure to 175° C., then vacuum was applied and the reaction was distilled for 10 minutes at 200° C. and 10 mm Hg. After vacuum distillation, the resin was cooled to 180° C. and 661.5 grams of ethyl lactate was added to make a 30% solids solution. A sample was taken for GPC MW<sub>w</sub>. After the resin solution reached room temperature, 236.25 grams of acetone was added to make a 24% solids solution. To this resin solution, 40% (w/w) DI water (472.5 g), was added under stirring. After all the water was added, the stirring was stopped and the solution was allowed to settle to form two separate top and bottom layers. The top layer was siphoned off (981.6 gl). Then one half the original amount of acetone (141.75 g) was added to the resin/bottom layer and it was stirred. One half the original amount of water (236.25 g) was added under stirring to again form 2 separate top and bottom layers. After allowing the mixture to settle, the top layer was siphoned off (683.0 g). Ethyl lactate was added to the resin/bottom layer, and the final solution was vacuum distilled at 75° C. and 25 mm Hg to remove residual water, acetone, and to achieve a 30% solids solution. The GPC MW<sub>w</sub> of the resin was 3876 and the dissolution rate was 677.6 Angstroms/sec. A photoresist was formulated as in example 4 and it's lithographic performance was far worse than any fractionated resin according to the present invention shown in examples 2, 4, and 12 to 15.

What we desire to claim is:

1. A method for producing a film forming novolak resin which comprises:

- condensing formaldehyde with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin condensation product, and then removing unreacted phenolic compounds;
- adding a photoresist solvent, thereby forming a solution of the novolak resin condensation product, then adding a water soluble organic polar solvent and water to the solution of the novolak resin condensation product, at a ratio of photoresist solvent:water soluble organic polar solvent:water of 1-9:1-5:3-7, and separating the solution into two layers, a top solution layer and a bottom solution layer, and then removing the top layer;
- adding a water soluble organic polar solvent and water to the bottom layer solution remaining after step b), in the ratio of water soluble organic polar solvent:water of 1:10 to 10:1, thereby separating the bottom layer solution from step b) into two layers, a top solution layer and a bottom solution layer, and then removing the top layer;
- removing any remaining water and water soluble organic polar solvent from the bottom solution layer resulting from step c), and thereby producing a film forming, fractionated novolak resin solution.

2. The method of claim 1, wherein in step a) the unreacted phenolic compounds are removed by distilling the novolak resin condensation product under atmospheric pressure at a temperature from about 100° C. to 175° C. and then under vacuum at a temperature of from about 175° C. to 200° C.



3. The method of claim 1, wherein in step b) the ratio of photoresist solvent:water soluble organic polar solvent:water is from 6-9:1-3:3-5.

4. The method of claim 1, wherein in step c) the ratio of water soluble organic polar solvent:water is from 2:8 to 8:2.

5. The method of claim 1, wherein in step c) the ratio of water soluble organic polar solvent:water is 3:7 to 7:3.

6. The method of claim 1, wherein the water soluble organic polar solvent is acetone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, ethylene glycol or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol.

7. The method of claim 1, wherein the photoresist solvent is propylene glycol methyl ether acetate, 3-methoxy-3-methyl butanol, 2-heptanone or a monooxymonocarboxylic acid ester.

8. The method of claim 1, where in said acid catalyst is oxalic acid, maleic acid, maleic anhydride, sulfuric acid or p-toluene sulfonic acid.

9. The method of claim 1, wherein the water soluble organic polar solvent is acetone or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol.

10. The method of claim 1, wherein the photoresist solvent is a monooxymonocarboxylic acid ester.

11. A method for producing a positive working photoresist composition having superior lithographic performance comprising:

- a) condensing formaldehyde with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin condensation product, and then removing unreacted phenolic compounds;
- b) adding a photoresist solvent, thereby forming a solution of the novolak resin condensation product, then adding a water soluble organic polar solvent and water to the solution of the novolak resin condensation product, at a ratio of photoresist solvent:water soluble organic polar solvent:water of 1-9:1-5:3-7, and separating the solution into two layers, a top solution layer and a bottom solution layer, and then removing the top layer;
- c) adding a water soluble organic polar solvent and water to the bottom layer solution remaining after step b), in the ratio of water soluble organic polar solvent:water of 1:10 to 10:1, thereby separating the bottom layer solution from step b) into two layers, a top solution layer and a bottom solution layer, and then removing the top layer;
- d) removing any remaining water and water soluble organic polar solvent from the bottom solution layer resulting from step c), and thereby producing a film forming, fractionated novolak resin solution;
- e) providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize a photoresist composition; 2) the film forming novolak resin solution resulting from step d); and 3) additional photoresist solvent, and thereby forming a positive working photoresist composition.

12. The method of claim 11, wherein in step a) the unreacted phenolic compounds are removed by distilling the novolak resin condensation product under atmospheric pressure at a temperature from about 100° C. to 175° C. and then under vacuum at a temperature of from about 175° C. to 200° C.

13. The method of claim 11, wherein in step b) the ratio of photoresist solvent:water soluble organic polar solvent:water is from 6-9:1-3:3-5.

14. The method of claim 11, wherein in step c) the ratio of water soluble organic polar solvent:water is from 2:8 to 8:2.

15. The method of claim 11, wherein in step c) the ratio of water soluble organic polar solvent:water is from 3:7 to 7:3.

16. The method of claim 11, wherein the water soluble organic polar solvent is acetone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, ethylene glycol or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol.

17. The method of claim 11, wherein the photoresist solvent is propylene glycol methyl ether acetate, 3-methoxy-3-methyl butanol, 2-heptanone or a monooxymonocarboxylic acid ester.

18. The method of claim 11, wherein said acid catalyst is oxalic acid, maleic acid, maleic anhydride, sulfuric acid, or p-toluene sulfonic acid.

19. The method of claim 11, wherein the water soluble organic polar solvent is acetone or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol.

20. The method of claim 11, wherein the photoresist solvent is a monooxymonocarboxylic acid ester.

21. A method for producing a semiconductor device by producing a photo-image on a substrate by coating a suitable substrate with a positive working photoresist composition said method comprising:

- a) condensing formaldehyde with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin condensation product, and then removing unreacted phenolic compounds;
- b) adding a photoresist solvent, thereby forming a solution of the novolak resin condensation product, then adding a water soluble organic polar solvent and water to the solution of the novolak resin condensation product, at a ratio of photoresist solvent:water soluble organic polar solvent:water of 1-9:1-5:3-7, and separating the solution into two layers, a top solution layer and a bottom solution layer, and then removing the top layer;
- c) adding a water soluble organic polar solvent and water to the bottom layer solution remaining after step b), in the ratio of water soluble organic polar solvent:water ratio of 1:10 to 10:1, thereby separating the bottom layer solution from step b) into two layers, a top solution layer and a bottom solution layer, and then removing the top layer;
- d) removing any remaining water and water soluble organic polar solvent from the bottom solution layer resulting from step c), and thereby producing a film forming, fractionated novolak resin solution;
- e) providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize a photoresist composition; 2) the film forming novolak resin solution resulting from step d); and 3) additional photoresist solvent, and thereby forming a positive working photoresist composition;
- f) coating a suitable substrate with the photoresist composition resulting from step e);
- g) heat treating the coated substrate resulting from step f) until substantially all of the photoresist solvent is removed; image-wise exposing the photosensitive composition and removing the image-wise exposed areas of such photoresist composition with a suitable developer.

22. The method of claim 21, wherein in step a) the unreacted phenolic compounds are removed by distilling the novolak resin condensation product under atmospheric pressure at a temperature from about 100° C. to 175° C. and then under vacuum at a temperature of from about 175° C. to 200° C.

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23. The method of claim 21, wherein in step b the ratio of photoresist solvent:water soluble organic polar solvent:water is from 6-9:1-3:3-5.

24. The method of claim 21, wherein in step c) the ratio of water soluble organic polar solvent is from 3:7 to 7:3. 5

25. The method of claim 21, wherein the water soluble organic polar solvent is acetone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, ethylene glycol or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol.

26. The method of claim 21, wherein the photoresist 10 solvent is propylene glycol methyl ether acetate, 3-methoxy-

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3-methyl butanol, 2-heptanone or a monooxymonocarboxylic acid ester.

27. The method of claim 21, wherein the acid catalyst is oxalic acid, maleic acid, maleic anhydride, sulfuric acid, or p-toluene sulfonic acid.

28. The method of claim 21, wherein the water soluble organic polar solvent is acetone or a C<sub>1</sub>-C<sub>3</sub> alkyl alcohol.

29. The method of claim 21, wherein the photoresist solvent is a monooxymonocarboxylic acid ester.

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